CERTIFICATION OF TRANSLATION

I, ***Moung-kyo Kim***, an employee of Y.P. LEE, MOCK & PARTNERS of Koryo Building, 1575-1 Seocho-dong, Seocho-gu, Seoul, Republic of Korea 137-875, hereby declare under penalty of perjury that I understand the Korean language and the English language; that I am fully capable of translating from Korean to English and vice versa; and that, to the best of my knowledge and belief, the statement in the English language in the attached translation of ***Korean Patent Application 10-2003-0025533*** consisting of 29 pages, have the same meanings as the statements in the Korean language in the original document, a copy of which I have examined.

Signed this 18st day of September 2008

Moung Kyo Kim

ABSTRACT

[Abstract of the Disclosure]

Provided is a method for forming a high dielectric film made of a metal oxide by sequentially depositing an oxygen-deficient metal oxide film and a metal oxide film using two-step atomic layer deposition (ALD). The oxygen-deficient metal oxide film made of a metal oxide with an oxygen content less than a stoichiometric amount is formed on a semiconductor substrate using an organic metal compound as a first reactant by ALD. The metal oxide film is formed on the oxygen-deficient metal oxide film using the first reactant and an oxidizing agent as a second reactant by ALD. Provided is also a method of forming a lanthanum oxide film by ALD, including: forming a first lanthanum oxide film with a composition of La_2O_x where $x<3$ on a semiconductor substrate and forming a second lanthanum oxide film with a composition of La_2O_3 on the first lanthanum oxide film. An alkoxide-based organic metal compound is used as a lanthanum source.

[Representative Drawing]

FIG. 1D

[Index]

lanthanum oxide film, organic metal compound, alkoxide, oxygen-deficient metal oxide film

SPECIFICATION

[Title of the Invention]

METHODS OF FORMING METAL THIN FILM, LANTHANUM OXIDE FILM, AND HIGH DIELECTRIC FILM FOR SEMICONDUCTOR DEVICE USING ATOMIC LAYER DEPOSITION

[Brief Description of the Drawings]

FIGS. 1A through 1D are sectional views that illustrate successive processes for a method of forming a high dielectric film according to a first embodiment of the present invention;

FIGS. 2A and 2B are gas pulsing diagrams that are applied in an atomic layer deposition (ALD) process for high dielectric film formation according to the present invention;

FIG. 3 is a graph showing variation in deposition rate of a lanthanum oxide film with temperature in an ALD process;

FIGS. 4A and 4B are sectional views that illustrate successive processes for a method of forming a high dielectric film according to a second embodiment of the present invention; and

FIG. 5 is a graph showing leakage current characteristics of the high dielectric film according to the second embodiment of the present invention.

< Explanation of Reference numerals designating the Major Elements of the Drawings >

10; semiconductor substrate	12; lower electrode
20; high dielectric film	22: oxygen-deficient metal oxide film
26; metal oxide film	110; semiconductor substrate
112; lower electrode	120; first dielectric film
130; second dielectric film	132; oxygen-deficient metal oxide film
136; metal oxide layer	

[Detailed Description of the Invention]

[Object of the Invention]

[Technical Field of the Invention and Related Art prior to the Invention]

The present invention relates to a method of manufacturing an integrated circuit, and more particularly, to methods of forming a metal thin film and a lanthanum oxide film. The present invention also relates to a method of forming a high dielectric film for improving electric properties of a capacitor in a semiconductor memory device.

As the degree of integration of semiconductor devices increases, more capacitance per unit surface area is being required in capacitors for Dynamic Random Access Memory (DRAM) devices. Hence, there have been suggested a method of increasing a surface area of a capacitor electrode by designing the electrode in a stack-type, a cylinder-type, a trench-type, and the like or by forming a hemispheric grain on the surface of the electrode, a method for decreasing a thickness of a dielectric film, and a method of using a high dielectric material or a ferroelectric material with a high dielectric constant as a dielectric film. Among these methods, the method of increasing a surface area of a capacitor electrode is not applicable any more because a surface area of the electrode has already reached at a possible maximal level. In the method of decreasing a thickness of a dielectric film, a capacitance increases with decrease of the thickness but a leakage current significantly increases. Therefore, this method also has a limitation in the application. With respect to the method of using a high dielectric material for a dielectric film, in the case of using a high dielectric material with a high dielectric constant such as Ta_2O_5, TiO_2, Al_2O_3, Y_2O_3, ZrO_2, and BST ((Ba, Sr)TiO_3), there arises a problem that polysilicon, which has been currently used as an electrode material, cannot be used any more. This is because as the thickness of a dielectric film decreases, tunneling occurs and thus a leakage current increases. In addition, the above illustrated high dielectric materials tend to react with polysilicon, whereby oxidation of polysilicon may occur or metal silicate may be generated. As a result, there arises a problem that the generated dielectric film serves as a low dielectric

layer. In order to solve this problem, incorporation of a nitride film between the high dielectric film and the polysilicon film is required.

As an example of one of the methods for increasing a capacitance per unit surface area of a capacitor, there is suggested a metal-insulator-metal (MIM) capacitor using a metal such as TiN and Pt with high work function, instead of polycrystalline silicon, as an electrode material. In the MIM capacitor, a metal oxide derived from a metal with a high oxygen affinity is mainly used as a dielectric film material. Examples of a metal oxide currently used as the dielectric film material for the MIM capacitor includes Ta_2O_5, Y_2O_3, HfO_2, Nb_2O_5, TiO_2, BaO, SrO, and BST.

Recent studies on La_2O_3, which has a high dielectric constant of 27 and a thermodynamic stability with silicon at a relatively high temperature of about 1,000 K, revealed that La_2O_3 has significant potential advantages as a metal oxide dielectric film material for a capacitor. Up until now, a La_2O_3 film has been mainly formed using evaporation or chemical vapor deposition (CVD).

However, actual application of the La_2O_3 film formed by evaporation or CVD to an integrated circuit is accompanied by following limitations. First, in order to use the La_2O_3 film as a dielectric film for a capacitor, excellent step coverage and uniform deposition thickness must be secured even at a three dimensional structure with a high step difference. However, the La_2O_3 film formed by evaporation has poor step coverage and thus cannot be used as a dielectric film for a capacitor. Second, in order to maintain high dielectric characteristics of the La_2O_3 film, the formation of a low dielectric layer between the La_2O_3 film and a lower electrode must be prevented. However, in the case of using a polysilicon electrode, formation of the La_2O_3 film by CVD allows for easy formation of lanthanum silicate at the interface between the La_2O_3 film and the polysilicon electrode, due to a high deposition temperature applied during the CVD. The formed lanthanum silicate serves as a low dielectric layer, thereby decreasing an electrostatic capacity.

[Technical Goal of the Invention]

The present invention provides a method of forming a metal thin film capable of preventing the formation of a low dielectric layer at the interface between the metal thin film and a lower electrode.

The present invention also provides a method of forming a lanthanum oxide film with a uniform thickness and excellent step coverage on a lower electrode with a high step difference due to a three dimensional structure.

The present invention also provides a method of forming a high dielectric film capable of improving electric properties of a capacitor in a semiconductor device by forming a lanthanum oxide film with a high dielectric constant. Therefore, excellent step coverage is secured and formation of a low dielectric layer can be prevented.

[Structure and Operation of the Invention]

In accordance with an aspect of the present invention, there is provided a method of forming a metal thin film. First, an oxygen-deficient metal oxide film made of a metal oxide with an oxygen content less than a stoichiometric amount is formed on a semiconductor substrate using an organic metal compound as a first reactant by atomic layer deposition (ALD). Then, a metal oxide film is formed on the oxygen-deficient metal oxide film using the first reactant and an oxidizing agent as a second reactant by ALD. The first reactant may be an alkoxide-based metal oxide.

In order to form the oxygen-deficient metal oxide film, the first reactant is fed onto the semiconductor substrate to form an adsorbed layer of the first reactant and then a byproduct on the semiconductor substrate is removed by means of purge. The adsorbed layer formation step and the purge step are repeated until the oxygen-deficient metal oxide film with a predetermined thickness is formed.

In order to form the metal oxide film, the first reactant is fed onto the semiconductor substrate having the oxygen-deficient metal oxide film thereon, to form a chemisorbed layer of the first reactant and then a byproduct of the reaction between the first reactant and the oxygen-deficient metal oxide film is removed. The second reactant is fed onto the chemisorbed layer to form the metal oxide film and then a

byproduct of the reaction between the second reactant and the chemisorbed layer is removed. The above-described steps are repeated until the metal oxide film with a predetermined thickness is formed.

The metal thin film formation method may further comprise annealing the oxygen-deficient metal oxide film. The annealing may be carried out immediately after the formation of the oxygen-deficient metal oxide film or the metal oxide film.

According to another aspect of the present invention, there is provided a method of forming a lanthanum oxide film. First, a first lanthanum oxide film with a composition of La_2O_x where $x<3$ is formed on a semiconductor substrate using an alkoxide-based organic metal compound as a first reactant by ALD. Then, a second lanthanum oxide film with a composition of La_2O_3 is formed on the first lanthanum oxide film using the first reactant and an oxidizing agent as a second reactant by ALD. The first reactant may be an alkoxide-based organic metal compound.

According to another aspect of the present invention, there is provided a method of forming a high dielectric film for a semiconductor device, comprising: forming a first dielectric film made of a first metal oxide on a semiconductor substrate and forming a second dielectric film made of a second metal oxide on the first dielectric film. In order to form the second dielectric film, an oxygen-deficient metal oxide film made of the second metal oxide with an oxygen content less than a stoichiometric amount is formed on the first dielectric film using an organic metal compound as a first reactant by ALD and then a metal oxide film is formed on the oxygen-deficient metal oxide film using the first reactant and an oxidizing agent as a second reactant by ALD. The first dielectric film may be made of Al_2O_3.

According to yet another aspect of the present invention, there is provided a method of forming a high dielectric film for a semiconductor device, comprising: forming a first dielectric film made of a metal oxide on a semiconductor substrate and forming a second dielectric film made of a lanthanum oxide on the first dielectric film. In order to form the second dielectric film, a first lanthanum oxide film with a composition of La_2O_x where $x<3$ is formed on the first dielectric film using an organic metal compound as a

first reactant by ALD and then a second lanthanum oxide film with a composition of La_2O_3 is formed on the first lanthanum oxide film using the first reactant and an oxidizing agent as a second reactant by ALD.

According to the present invention, two-step ALD of forming the oxygen-deficient metal oxide film and the metal oxide film is carried out to form a high dielectric film for a semiconductor device. The high dielectric film formed according to the present invention has excellent step coverage and good uniformity even at a wide area. Furthermore, a precise control of a film thickness in a fine unit can be accomplished. Therefore, a high dielectric film with a uniform thickness and excellent step coverage can be formed on a lower electrode with high step difference due to a three dimensional structure. In addition, because the formation of a low dielectric layer can be prevented by forming a metal oxide film with a high dielectric constant, electric properties of a capacitor are improved.

FIGS. 1A through 1D are sectional views that illustrate successive processes for a method of forming a high dielectric film according to a first embodiment of the present invention.

Referring to FIG. 1A, a lower electrode 12 is formed on a semiconductor substrate 10. The lower electrode 12 may be made of a metal nitride or a noble metal. For example, the lower electrode 12 may be made of TiN, TaN, WN, Ru, Ir, or Pt. In the case of forming a non-MIM capacitor, the lower electrode 12 may also be made of doped polysilicon. In this case, in order to prevent the lower electrode 12 from being oxidized during a subsequent annealing process, a silicon nitride film (not shown) is formed on the lower electrode 12 by rapid thermal nitridation (RTN) of the surface of the lower electrode 12.

Then, an oxygen-deficient metal oxide film 22 is formed to a thickness of about 5 to 30Å on the lower electrode 12 using an organic metal compound as a first reactant by an atomic layer deposition (ALD) process. Preferably, the ALD process for formation of the oxygen-deficient metal oxide film 22 is carried out at a temperature range of about 200 to 350℃.

The oxygen-deficient metal oxide film 22 is made of a metal oxide with an oxygen content less than a stoichiometric amount. In the case of forming a high dielectric film made of a lanthanum oxide, the oxygen-deficient metal oxide film 22 is a lanthanum oxide film with a composition of La_2O_x where $x<3$.

Examples of the first reactant for formation of the oxygen-deficient metal oxide film 22 made of a lanthanum oxide include tris(1-n-propoxy-2-methyl-2-propoxy)lanthanum (III) ($La(NPMP)_3$), tris(2-ethyl-1-n-propoxy-2-butoxy)lanthanum (III) ($La(NPEB)_3$), lanthanum (III) ethoxide ($La(OCH_2H_5)_3$), tris(6-ethyl-2,2-dimethyl-3,5-decanedionato)lanthanum (III) ($La(EDMDD)_3$), tris(dipivaloylmethanate)lanthanum (III) ($La(DPM)_3$), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanum (III) ($La(TMHD)_3$), lanthanum (III) acetylacetonate ($La(acac)_3$), and tris(ethylcyclopentadienyl)lanthanum (III) ($La(EtCp)_3$).

Preferably, the first reactant is an alkoxide-based metal oxide such as $La(NPMP)_3$, $La(NPEB)_3$, and $La(OC_2H_5)_3$. More preferably, the first reactant is $La(NPMP)_3$. In order to use solid $La(NPMP)_3$ in an ALD process for formation of a high dielectric film according to the present invention, first, $La(NPMP)_3$ is dissolved in a solvent such as ethylcyclohexane and then fed into a vaporizer. The $La(NPMP)_3$ is vaporized in the vaporizer and then fed into an ALD chamber.

The oxygen-deficient metal oxide film 22 is formed using only the first reactant as a main source by ALD. That is, one ALD cycle for formation of the oxygen-deficient metal oxide 22 includes forming feeding the first reactant onto the semiconductor substrate 10 having the lower electrode 12 thereon, to form an adsorbed layer of the first reactant including a chemisorbed layer and a physisorbed layer and removing a byproduct on the semiconductor substrate 10 by means of inert gas purge. The oxygen-deficient metal oxide film 22 with a desired thickness is formed by repeating one ALD cycle including the first reactant adsorption step and the inert gas purge step several times.

As described above, the oxygen-deficient metal oxide film 22 is formed by using an organic metal compound such as a lanthanum source and a purge gas. By doing

so, the oxidation of the lower electrode 12 is prevented. That is, because an oxidizing agent is not used during the deposition for the formation of the oxygen-deficient metal oxide film 22, the oxidation of the lower electrode 12 is prevented. Also, the oxygen-deficient metal oxide film 22 serves as a film for preventing the diffusion of a gaseous oxidizing agent used during a subsequent deposition process. Therefore, the oxidation of the lower electrode 12 can be prevented.

Referring to FIG. 1B, the oxygen-deficient metal oxide film 22 is annealed under an oxygen-containing gas atmosphere or a vacuum atmosphere. Such annealing is carried out for removing impurities, for example, carbon, which may be contained in the oxygen-deficient metal oxide film 22, but may be omitted in some cases. Such annealing may also be carried out after the completion of a subsequent high dielectric film deposition process, unlike FIG. 1B.

The annealing may be performed under a gas atmosphere such as O_2, N_2, or O_3. Preferably, the annealing is carried out at a temperature range of about 300 to 800℃.

Referring to FIG. 1C, a metal oxide film 26 is formed on the oxygen-deficient metal oxide film 22 using the above first reactant and an oxidizing agent as a second reactant by ALD. Preferably, the ALD process for the formation of the metal oxide film 26 is carried out at a temperature range of about 200 to 350℃.

In the case of forming a high dielectric film made of a lanthanum oxide, the metal oxide film 26 has a composition of La_2O_3. Examples of the first reactant for formation of the metal oxide film 26 made of a lanthanum oxide include $La(NPMP)_3$, $La(NPEB)_3$, $La(OCH_2H_5)_3$, $La(EDMDD)_3$, $La(DPM)_3$, $La(TMHD)_3$, $La(acac)_3$, and $La(EtCp)_3$. The first reactant is preferably an alkoxide-based metal oxide and more preferably $La(NPMP)_3$. As described previously with reference to FIG. 1B, $La(NPMP)_3$ is fed into a vaporizer in a liquid state and then vaporized in the vaporizer before being fed into an ALD chamber. A lanthanum oxide film formed at a relatively low temperature of about 200 to 350℃ by ALD has step coverage characteristics equal or superior to that formed by CVD. In addition, because a relatively low temperature is used in the ALD process, formation of a low dielectric layer at the interface between the lower electrode 12 and

the high dielectric film can be prevented. Also, because the first reactant of an organic compound and the second reactant of an oxidizing agent are alternately fed into a process chamber in the ALD process, the gas phase reaction of the organic metal compound fundamentally does not occur and the ALD is carried out in a self-limiting manner by the surface reaction of the reactants. Therefore, a lanthanum oxide film formed by the ALD process has excellent step coverage and good uniformity even at a wide area. In addition, precise film thickness control can be accomplished to a several Å unit.

The oxidizing agent as the second reactant may be O_3, O_2, plasma O_2, H_2O, or N_2O. Preferably, the second reactant is O_3. By using O_3 as the second reactant, incorporation of impurities into the metal oxide film 26 is prevented and step coverage of the metal oxide film 26 is improved.

The metal oxide film 26 is formed using the first and second reactants as a main source by ALD. Here, one ALD cycle for the formation of the metal oxide film 26 includes the following steps. First, the first reactant is fed onto the semiconductor substrate 10 having the oxygen-deficient metal oxide film 22 thereon, to thereby form a chemisorbed layer of the first reactant. Then, a byproduct of the reaction between the first reactant and the oxygen-deficient metal oxide film is removed by inert gas purge. After the byproduct removal, the second reactant is fed onto the chemisorbed layer of the first reactant to form the metal oxide film. Then, a byproduct of the reaction between the second reactant and the chemisorbed layer is removed by inert gas purge. The one ALD cycle including the above-described steps is repeated several times until the metal oxide film 26 with a desired thickness is formed.

As described previously with reference to FIG. 1B, in a case wherein the annealing is omitted immediately after the formation of the oxygen-deficient metal oxide film 22, the annealing is carried out immediately after the formation of the metal oxide film 26, as shown in FIG. 1D. This completes the high dielectric film 20. The detailed description of the annealing is as described above with reference to FIG. 1B.

FIGS. 2A and 2B are gas pulsing diagrams that are applied in the ALD process for high dielectric film formation according to the present invention. In detail, FIG. 2A is a gas pulsing diagram that is applied in the ALD process for the formation of the oxygen-deficient metal oxide film 22 and FIG. 2B is a gas pulsing diagram that is applied in the ALD process for the formation of the metal oxide film 26.

Referring to FIG. 2A, one ALD cycle for the formation of the oxygen-deficient metal oxide film 22 includes feeding the first reactant onto the semiconductor substrate 10 having the lower electrode 12 thereon, to form an adsorbed layer of the first reactant (step A) and removing a byproduct of step A by means of purge with a first purge gas, i.e., an inert gas (step B). Steps A and B are repeated several times until the oxygen-deficient metal oxide film 22 with a predetermined thickness is formed. Here, the second reactant such as an oxidizing agent and a second purge gas for removal of a byproduct of the reaction using the second reactant are not used.

Referring to FIG. 2B, one ALD cycle for the formation of the metal oxide film 26 includes feeding the first reactant onto the semiconductor substrate 10 having the oxygen-deficient metal oxide film 22 thereon, to form a chemisorbed layer of the first reactant (step C), removing a byproduct of the step C by means of purge with the first purge gas, i.e., an inert gas (step D), feeding the second reactant onto the chemisorbed layer of the first reactant to form the metal oxide film (step E), and removing a byproduct of step E by means of purge with the second purge gas, i.e., an inert gas. Steps C through F are repeated several times until the metal oxide film 26 with a predetermined thickness is formed.

FIG. 3 is a graph showing variation in deposition rate of a lanthanum oxide film with temperature in an ALD process in order to evaluate the deposition rate of the lanthanum oxide film suitable for the high dielectric film formation method according to the present invention.

For the evaluation of FIG. 3, a La_2O_3 film was formed by ALD according to the gas pulsing diagram as shown in FIG. 2B at various temperature conditions. Here, $La(NPMP)_3$ was used as the first reactant, O_3 as the second reactant, and Ar as the first

and second purge gases. In each ALD cycle, steps C, D, E, and F were carried out for 0.02, 5, 5, and 5 seconds, respectively. The thickness of the La_2O_3 film after total 100 cycles of ALD was measured.

According to the result shown in FIG. 3, the thickness of the La_2O_3 film slowly increases at a temperature range of 200 to 350℃ and thus the deposition rate with increase of a deposition temperature is almost constant. Meanwhile, at more than 350℃, as a deposition temperature increases, the deposition rate rapidly increases due to degradation of source gases. Judging from the deposition rate tendency according to an increase of a deposition temperature as shown in FIG. 3, it can be seen that the La_2O_3 film can be deposited by ALD at about 350℃ or less.

FIGS. 4A and 4B are sectional views that illustrate successive processes for a method of forming a high dielectric film according to a second embodiment of the present invention. The second embodiment is almost the same as the first embodiment except that before forming an oxygen-deficient metal oxide film 132 on a lower electrode 112, a first dielectric film 120 made of a material different from a material for the oxygen-deficient metal oxide film 132 is further formed. The detailed description thereof is as follows.

Referring to FIG. 4A, as described above with reference to FIG. 1A, a lower electrode 112 is formed on a semiconductor substrate 110.

Then, the first dielectric film 120 made of a first metal oxide is formed on the lower electrode 112. The first dielectric film 120 serves as an oxygen blocking film for preventing the oxidation of the lower electrode 112 during subsequent dielectric film annealing. In particular, in a case where the lower electrode 120 is made of a metal nitride or a noble metal, oxidation of the lower electrode 112, which may occur during the subsequent dielectric film annealing, can be efficiently prevented.

Preferably, the first dielectric film 120 is made of Al_2O_3. The first dielectric film 120 may be formed to a thickness of about 30 to 60Å.

The first dielectric film 120 may be formed by CVD or ALD. In the case of forming the first dielectric film 120 made of Al_2O_3 using CVD, deposition may be

performed using trimethyl aluminum (TMA) and H_2O at a temperature range of about 400 to 500℃ under a pressure of about 1 to 5 Torr.

In the case of forming the first dielectric film 120 made of Al_2O_3 using ALD, deposition may be performed using TMA as a first reactant and O_3 as a second reactant at a temperature range of about 250 to 400℃ under a pressure of about 1 to 5 Torr. The deposition and purging processes are repeated until an Al_2O_3 film with a desired thickness is formed. The first reactant for the formation of the Al_2O_3 film may be $AlCl_3$, $AlH_3N(CH_3)_3$, $C_6H_{15}AlO$, $(C_4H_9)_2AlH$, $(CH_3)_2AlCl$, $(C_2H_5)_3Al$, or $(C_4H_9)_3Al$, except for TMA. The second reactant may be H_2O, plasma N_2O, or plasma O_2, which can serve as an activated oxidizing agent.

Referring to FIG. 4B, a second dielectric film 130 made of a second metal oxide is formed on the first dielectric film 120. The second metal oxide is different from the first metal oxide, for example, a lanthanum oxide.

The second dielectric film 130 is formed by sequentially depositing an oxygen-deficient metal oxide film 132 and a metal oxide film 136 on the first dielectric film 120, as described above with reference to FIGS. 1A through 1D. The detailed descriptions of the formation of the oxygen-deficient metal oxide film 132 and the metal oxide film 136 are as described above with reference to FIGS. 1A through 1D.

FIG. 5 is a graph showing an evaluation result (•) of leakage current characteristics of a high dielectric film having a dual film structure of the first dielectric film 120 and the second dielectric film 130 formed on the lower electrode 112 according to the second embodiment of the present invention.

For the evaluation of leakage current characteristics of FIG. 5, a first dielectric film made of Al_2O_3 was formed to a thickness of 30Å on a lower electrode made of TiN and then a second dielectric film made of La_2O_3 was formed to a thickness of 30Å on the first dielectric film. Here, a deposition temperature was set to 300℃. A TiN upper electrode was formed on the Al_2O_3/La_2O_3 dual film and then photolithography and etching were performed to thereby complete a capacitor. The leakage current characteristics of the completed capacitor were evaluated.

As comparative examples, the leakage current characteristics of a dielectric film (■) made of only Al_2O_3 with a thickness of 50Å and a dielectric film (▲) having a dual film structure of an Al_2O_3 film with a thickness of 30Å and a HfO_2 film with a thickness of 30Å were also shown in FIG. 5. Except for the above-described conditions, other conditions of the control examples were the same as in the case of the present invention (●).

According to the results of FIG. 5, the high dielectric film made of Al_2O_3/La_2O_3 according to the present invention has a relatively low equivalent oxide film thickness (Toxeq) of 28.5Å, and thus exhibits sufficiently high dielectric characteristics. In addition, the Al_2O_3/La_2O_3 dielectric film has a take-off voltage of about 2.0 V, which is similar to the take-off voltage of the Al_2O_3/HfO_2 dielectric film, and thus exhibits good leakage current characteristics.

[Effect of the Invention]

As apparent from the above description, the high dielectric film for a semiconductor device according to the present invention is formed using an organic metal compound as a metal source by ALD. In particular, in order to minimize the formation of a low dielectric layer at the interface between the lower electrode and the high dielectric film, at an early stage of the formation of the high dielectric film, the oxygen-deficient metal oxide film is formed using an organic metal compound, preferably an alkoxide-based organic metal compound, as a main source by ALD. Thereafter, in order to prevent the incorporation of impurities into the high dielectric film and improve step coverage, the metal oxide film is formed on the oxygen-deficient oxide film using an organic metal compound and an oxidizing agent as a main source.

The metal oxide film deposited by ALD according to the present invention has equal or superior step coverage and can be formed at a lower deposition temperature, when compared to a thin film deposited by CVD. Therefore, the formation of a low dielectric layer between the lower electrode and the high dielectric film is prevented. Also, because a metal source and an oxidizing agent are alternately fed into an ALD

process chamber, the gas phase reaction of the metal source fundamentally does not occur and the ALD is carried out in a self-limiting manner by the reaction of the surface saturated with the sources fed into the process chamber. Therefore, the metal oxide film formed by the ALD process has excellent step coverage and good uniformity even at a wide area. In addition, precise film thickness control of a fine unit level can be accomplished.

Therefore, according to the present invention, a high dielectric film with excellent step coverage and uniform thickness can be formed on a lower electrode with high step difference by a three dimensional structure. In addition, because the formation of a low dielectric layer can be prevented by forming a metal oxide film with a high dielectric constant, the electric properties of a capacitor can be improved.

While the present invention has been particularly shown and described with reference to exemplary embodiments thereof, it will be understood by those of ordinary skill in the art that various changes in form and details may be made therein without departing from the spirit and scope of the present invention as defined by the following claims.

What is claimed is:

1. A method of forming a metal thin film, comprising:

(a) forming an oxygen-deficient metal oxide film made of a metal oxide with an oxygen content less than a stoichiometric amount on a semiconductor substrate using an organic metal compound as a first reactant by atomic layer deposition (ALD); and

(b) forming a metal oxide film on the oxygen-deficient metal oxide film using the first reactant and an oxidizing agent as a second reactant by ALD.

2. The method according to claim 1, wherein the first reactant is an alkoxide-based metal oxide.

3. The method according to claim 1, wherein the first reactant is a lanthanum-containing compound.

4. The method according to claim 3, wherein the first reactant is selected from the group consisting of tris(1-n-propoxy-2-methyl-2-propoxy)lanthanum (III) ($La(NPMP)_3$), tris(2-ethyl-1-n-propoxy-2-butoxy)lanthanum (III) ($La(NPEB)_3$), lanthanum (III) ethoxide ($La(OCH_2H_5)_3$), tris(6-ethyl-2,2-dimethyl-3,5-decanedionato)lanthanum (III) ($La(EDMDD)_3$), tris(dipivaloylmethanate)lanthanum (III) ($La(DPM)_3$), tris(2,2,6,6-tetramethyl-3,5-heptanedionato)lanthanum (III) ($La(TMHD)_3$), lanthanum (III) acetylacetonate ($La(acac)_3$), and tris(ethylcyclopentadienyl)lanthanum (III) ($La(EtCp)_3$).

5. The method according to claim 1, wherein step (a) comprises:

(a-1) feeding the first reactant onto the semiconductor substrate to form an adsorbed layer of the first reactant;

(a-2) removing a byproduct of step (a-1) by means of purge; and

(a-3) repeating steps (a-1) and (a-2) until the oxygen-deficient metal oxide film with a predetermined thickness is formed.

6. The method according to claim 1, wherein the oxygen-deficient metal oxide film has a thickness of 5 to 30Å.

7. The method according to claim 1, wherein step (b) comprises:

(b-1) feeding the first reactant onto the semiconductor substrate having the oxygen-deficient metal oxide film thereon, to form a chemisorbed layer of the first reactant;

(b-2) feeding the second reactant onto the chemisorbed layer to form the metal oxide film; and

(b-3) repeating steps (b-1) and (b-2) until the metal oxide film with a predetermined thickness is formed.

8. The method according to claim 7, wherein the second reactant is selected from the group consisting of O_3, O_2, plasma O_2, H_2O, and N_2O.

9. The method according to claim 7, further comprising removing a byproduct after step (b-1) and removing a byproduct after step (b-2).

10. The method according to claim 9, wherein the steps of removing the byproducts are carried out by means of inert gas purge.

11. The method according to claim 1, wherein steps (a) and (b) are carried out at a temperature range of 200 to 350℃.

12. The method according to claim 1, further comprising annealing the oxygen-deficient metal oxide film.

13. The method according to claim 12, wherein the annealing is carried out immediately after step (a) or (b)

14. The method according to claim 12, wherein the annealing is carried out at a temperature range of 300 to 800℃.

15. The method according to claim 12, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O_2, N_2, and O_3, or under a vacuum atmosphere.

16. A method of forming a lanthanum oxide film, comprising:

(a) forming a first lanthanum oxide film with a composition of La_2O_x where $x<3$ on a semiconductor substrate using an alkoxide-based organic metal compound as a first reactant by ALD; and

(b) forming a second lanthanum oxide film with a composition of La_2O_3 on the first lanthanum oxide film using the first reactant and an oxidizing agent as a second reactant by ALD.

17. The method according to claim 16, wherein the first reactant is selected from the group consisting of $La(NPMP)_3$, $La(NPEB)_3$, and $La(OC_2H_5)_3$.

18. The method according to claim 16, wherein step (a) comprises:

(a-1) feeding the first reactant onto the semiconductor substrate to form an adsorbed layer of the first reactant;

(a-2) removing a byproduct of step (a-1) by means of purge; and

(a-3) repeating steps (a-1) and (a-2) until the first lanthanum oxide film with a predetermined thickness is formed.

19. The method according to claim 18, wherein the first lanthanum oxide film has a thickness of 5 to 30Å.

20. The method according to claim 16, wherein step (b) comprises:

(b-1) feeding the first reactant onto the semiconductor substrate having the first lanthanum oxide film thereon, to form a chemisorbed layer of the first reactant;

(b-2) feeding the second reactant onto the chemisorbed layer to form the second lanthanum oxide film; and

(b-3) repeating steps (b-1) and (b-2) until the second lanthanum oxide film with a predetermined thickness is formed.

21. The method according to claim 20, wherein the second reactant is selected from the group consisting of O_3, O_2, plasma O_2, H_2O, and N_2O.

22. The method according to claim 20, further comprising removing a byproduct after step (b-1) and removing a byproduct after step (b-2).

23. The method according to claim 22, wherein the steps of removing the byproducts are carried out by means of inert gas purge.

24. The method according to claim 16, wherein steps (a) and (b) are carried out at a temperature range of 200 to 350℃.

25. The method according to claim 16, further comprising annealing the first lanthanum oxide film.

26. The method according to claim 25, wherein the annealing is carried out immediately after step (a) or (b)

27. The method according to claim 25, wherein the annealing is carried out at a temperature range of 300 to 800℃.

28. The method according to claim 25, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O_2, N_2, and O_3, or under a vacuum atmosphere.

29. A method of forming a high dielectric film, comprising:

(a) forming a first dielectric film made of a first metal oxide on a semiconductor substrate; and

(b) forming a second dielectric film made of a second metal oxide on the first dielectric film,

step (b) comprising:

(b-1) forming an oxygen-deficient metal oxide film made of the second metal oxide with an oxygen content less than a stoichiometric amount on the first dielectric film using an organic metal compound as a first reactant by ALD; and

(b-2) forming a metal oxide film on the oxygen-deficient metal oxide film using the first reactant and an oxidizing agent as a second reactant by ALD.

30. The method according to claim 29, wherein the first dielectric film is made of Al_2O_3.

31. The method according to claim 29, wherein the first dielectric film is formed by chemical vapor deposition (CVD) or ALD.

32. The method according to claim 29, wherein the first dielectric film has a thickness of 30 to 60Å.

33. The method according to claim 29, wherein the first reactant is an alkoxide-based metal oxide.

34. The method according to claim 29, wherein step (b-1) comprises:

feeding the first reactant onto the first dielectric film to form an adsorbed layer of the first reactant;

removing a byproduct on the semiconductor substrate by means of purge; and

repeating the adsorbed layer formation step and the purge step several times.

35. The method according to claim 29, wherein the oxygen-deficient metal oxide film has a thickness of 5 to 30Å.

36. The method according to claim 29, wherein step (b-2) comprises:

feeding the first reactant onto the semiconductor substrate having the oxygen-deficient metal oxide film thereon, to form a chemisorbed layer of the first reactant;

feeding the second reactant onto the chemisorbed layer to form the metal oxide film; and

repeating the chemisorbed layer formation step and the metal oxide film formation step several times.

37. The method according to claim 36, wherein the second reactant is selected from the group consisting of O_3, O_2, plasma O_2, H_2O, and N_2O.

38. The method according to claim 36, further comprising removing a byproduct after the formation of the chemisorbed layer of the first reactant and removing a byproduct after the formation of the metal oxide film.

39. The method according to claim 38, wherein the steps of removing the byproducts are carried out by means of inert gas purge.

40. The method according to claim 29, wherein steps (b-1) and (b-2) are carried out at a temperature range of 200 to 350℃.

41. The method according to claim 29, further comprising annealing the oxygen-deficient metal oxide film.

42. The method according to claim 41, wherein the annealing is carried out immediately after step (b-1) or (b-2).

43. The method according to claim 41, wherein the annealing is carried out at a temperature range of 300 to 800℃.

44. The method according to claim 41, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O_2, N_2, and O_3, or under a vacuum atmosphere.

45. A method of forming a high dielectric film, comprising:

(a) forming a first dielectric film made of a metal oxide on a semiconductor substrate; and

(b) forming a second dielectric film made of a lanthanum oxide on the first dielectric film,

step (b) comprising:

(b-1) forming a first lanthanum oxide film with a composition of La_2O_x where $x<3$ on the first dielectric film using an organic metal compound as a first reactant by ALD; and

(b-2) forming a second lanthanum oxide film with a composition of La_2O_3 on the first lanthanum oxide film using the first reactant and an oxidizing agent as a second reactant by ALD.

46. The method according to claim 45, wherein the first dielectric film is made of Al_2O_3.

47. The method according to claim 45, wherein the first dielectric film is formed by CVD or ALD.

48. The method according to claim 45, wherein the first dielectric film has a thickness of 30 to 60Å.

49. The method according to claim 45, wherein the first reactant is selected from the group consisting of $La(NPMP)_3$, $La(NPEB)_3$, $La(OCH_2H_5)_3$, $La(EDMDD)_3$, $La(DPM)_3$, $La(TMHD)_3$, $La(acac)_3$, and $La(EtCp)_3$.

50. The method according to claim 45, wherein step (b-1) comprises:

feeding the first reactant onto the first dielectric film to form an adsorbed layer of the first reactant;

removing a byproduct on the semiconductor substrate by means of purge; and

repeating the adsorbed layer formation step and the purge step several times.

51. The method according to claim 45, wherein the first lanthanum oxide film has a thickness of 5 to 30Å.

52. The method according to claim 45, wherein step (b-2) comprises:

feeding the first reactant onto the semiconductor substrate having the first lanthanum oxide film thereon, to form a chemisorbed layer of the first reactant;

feeding the second reactant onto the chemisorbed layer to form the second lanthanum oxide film; and

repeating the chemisorbed layer formation step and the second lanthanum oxide film formation step several times.

53. The method according to claim 52, wherein the second reactant is

selected from the group consisting of O_3, O_2, plasma O_2, H_2O, and N_2O.

54. The method according to claim 52, further comprising removing a byproduct after the formation of the chemisorbed layer of the first reactant and removing a byproduct after the formation of the second lanthanum oxide film.

55. The method according to claim 54, wherein the steps of removing the byproducts are carried out by means of inert gas purge.

56. The method according to claim 45, wherein steps (b-1) and (b-2) are carried out at a temperature range of 200 to 350℃.

57. The method according to claim 45, further comprising annealing the first lanthanum oxide film.

58. The method according to claim 57, wherein the annealing is carried out immediately after step (b-1) or (b-2)

59. The method according to claim 57, wherein the annealing is carried out at a temperature range of 300 to 800℃.

60. The method according to claim 57, wherein the annealing is carried out under an atmosphere of a gas selected from the group consisting of O_2, N_2, and O_3, or under a vacuum atmosphere.

FIG. 1A

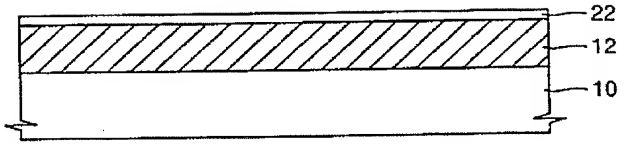


FIG. 1B

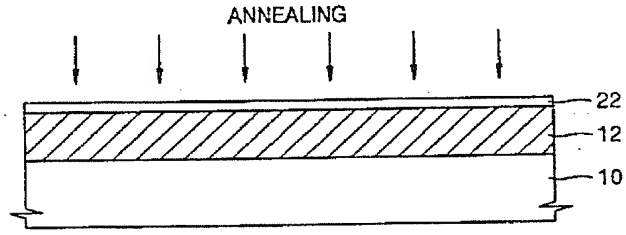


FIG. 1C

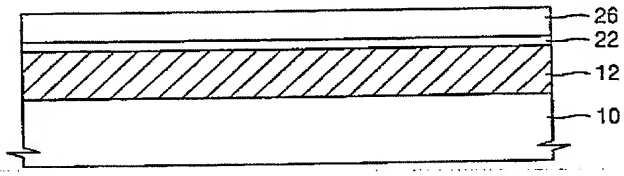


FIG. 1D

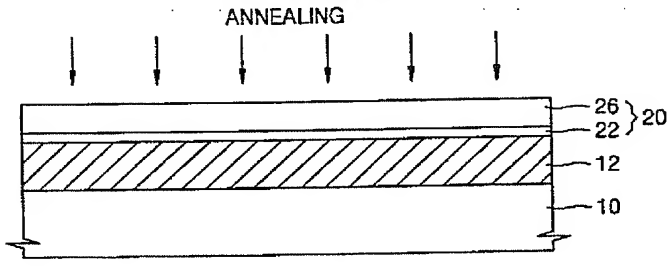


FIG. 2A

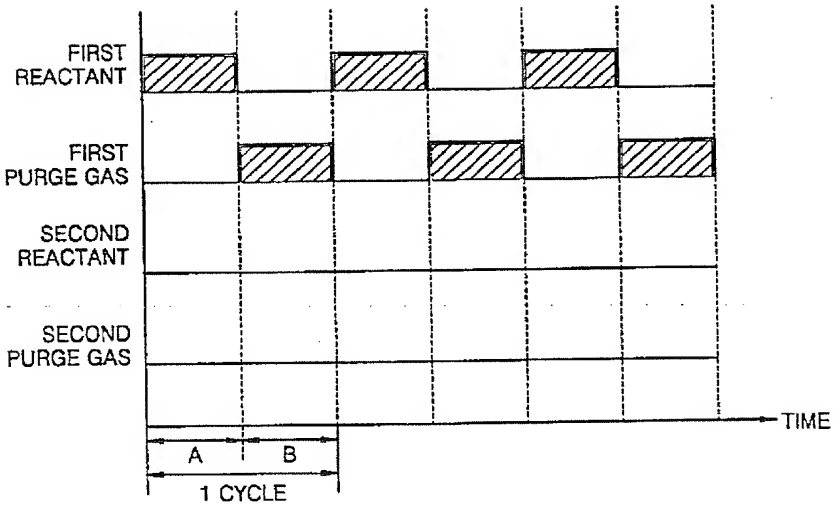

FIRST REACTANT
FIRST PURGE GAS
SECOND REACTANT
SECOND PURGE GAS
TIME
A
B
1 CYCLE

FIG. 2B

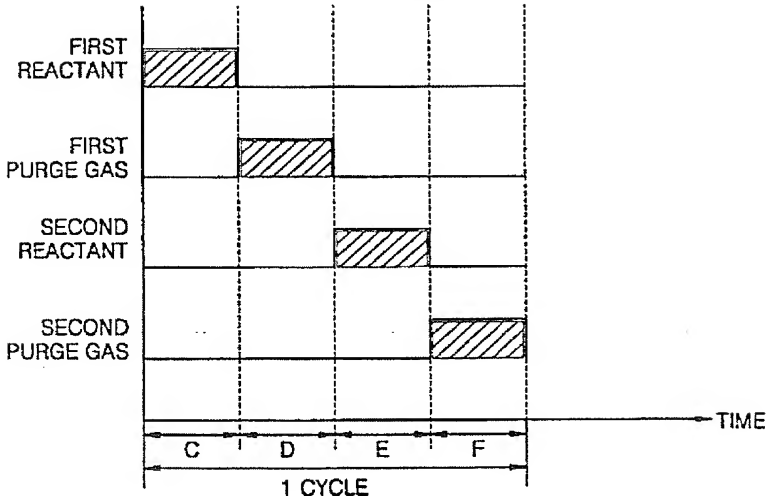

FIRST REACTANT
FIRST PURGE GAS
SECOND REACTANT
SECOND PURGE GAS
TIME
C
D
E
F
1 CYCLE

FIG. 3

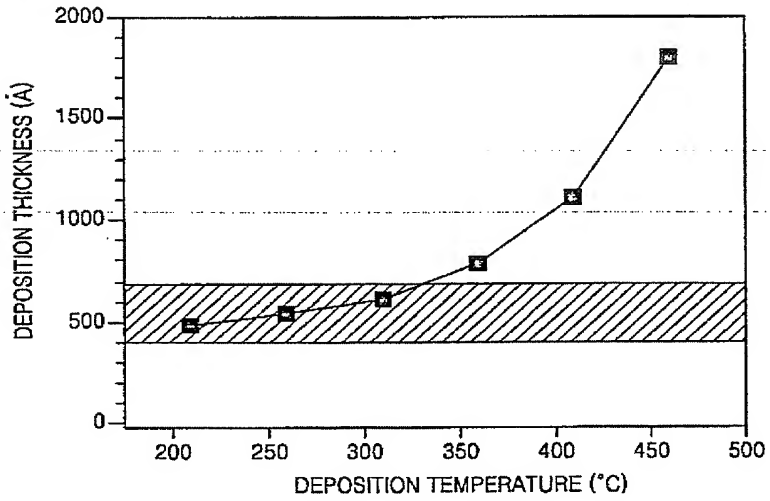

2000
1500
1000
500
0
DEPOSITION THICKNESS (Å)
200
250
300
350
400
450
500
DEPOSITION TEMPERATURE (°C)

FIG. 4A

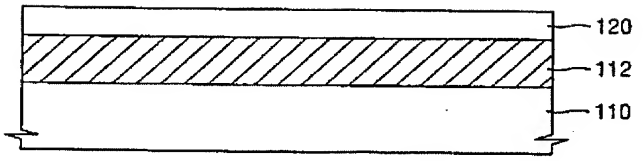


FIG. 4B

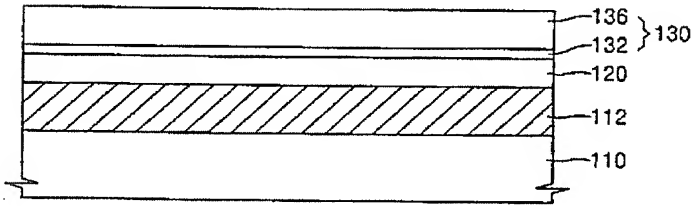
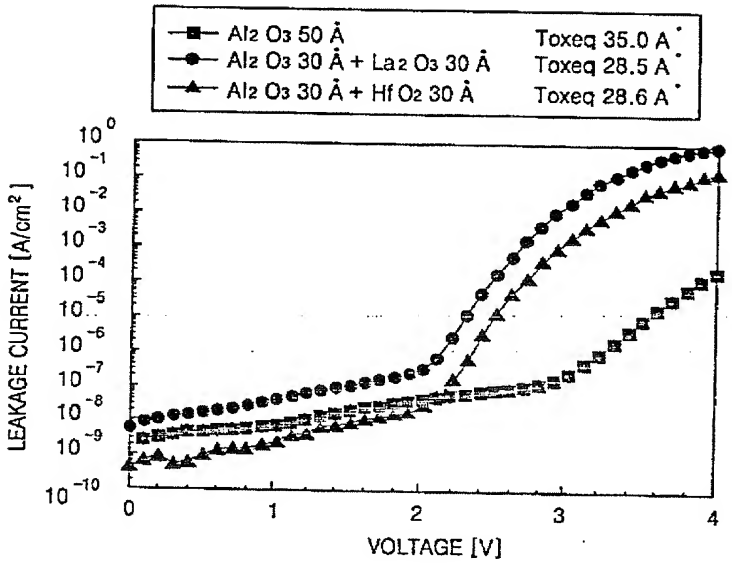


FIG. 5


Al2 O3 50 Å
Al2 O3 30 Å + La2 O3 30 Å
Al2 O3 30 Å + Hf O2 30 Å
Toxeq 35.0 Å
Toxeq 28.5 Å
Toxeq 28.6 Å
LEAKAGE CURRENT [A/cm²]
VOLTAGE [V]